

ISOMERIZATION AND ADDUCTION OF HYDROGEN DONOR SOLVENTS UNDER CONDITIONS OF COAL LIQUEFACTION

Donald C. Cronauer
Douglas M. Jewell
Yatish T. Shah
Rajiv J. Modi
K. S. Seshadri

Gulf Research & Development Company
P.O. Drawer 2038
Pittsburgh, PA 15230

INTRODUCTION

Fundamental studies on the chemistry of coal liquefaction have shown that the structure of solvent molecules can determine the nature of liquid yields that result at any particular set of reaction conditions. One approach to understanding this chemistry is to liquefy coal using well-defined solvents or to study reactions of solvents with pure compounds which may represent bond types that are likely present in coal (1). It is postulated that coal liquefaction is initiated by thermal activation to form free radicals which abstract hydrogen from any readily available source. The solvent may, therefore, function as a direct source of hydrogen (donor), indirect source of hydrogen (hydrogen-transfer agent), or may directly react with the coal (adduction). The actual role of solvent thus becomes a significant parameter.

Earlier studies have measured the reactivity of both hydrocarbon (1) and non-hydrocarbon (2) acceptors with good donor solvents (tetralin, hydrophenanthrenes), and poor donors (mesitylene). Although the primary role of solvents was observed to be the stabilization of acceptor radicals, appreciable levels of solvent rearrangement (isomerization), polymerization, and adduction also occurred. Herein, these aspects of solvent chemistry have been pursued with the use of ^{13}C labeling techniques to understand the specific reactions.

EXPERIMENTAL

The experimental procedure to carry out the solvent-acceptor reactions has been described earlier (1,2).

Specifically labeled ^{13}C -octahydrophenanthrene was synthesized by Dr. E. J. Eisenbraun, details of which will be described elsewhere.

REACTIVITY OF HYDROAROMATICS

Background

Due to the relative ease and reversibility of hydrogenation-dehydrogenation of hydroaromatics, they have been used extensively either as a source or agent for placing hydrogen in hydrogen-deficient species, such as coal.⁽³⁾ The assumption has frequently been made that hydroaromatics in the solvents used for this purpose contained the (ideal) six-membered ring while little effort has been directed to determining the isomeric forms. It is known that methyl indanes are essentially stable to hydrogen-transfer as compared to tetralin. Due to difficulties in adequately measuring the concentrations of isomeric structures, the above assumption may not be typically valid.

Tetralin has been shown to undergo thermal dehydrogenation to naphthalene and rearrangement to methylindane in either the absence or presence of free radicals (1). This implies that it may not be valid to assume that hydrogen transfer will be quantitative even in the presence of a large excess of donor solvent. Sym-octahydrophenanthrene (H_8Ph) would be expected to follow the same rearrangement-dehydrogenation reactions as tetralin, except with more isomer and product possibilities (see Figure 1). The kinetics of these reactions will be briefly discussed.

STRUCTURAL FEATURES OF HYDROPHENANTHRENES

The initial indication that hydrophenanthrenes isomerize was the observation of numerous GLC peaks with identical parent ions but different fragment ions in their mass spectra. Compounds with methyl substituents always have more intense M^+-15 ions than those with unsubstituted six-membered rings. Considering the complexity of the total reaction mixtures, liquid chromatography (HPLC) was used to concentrate more discrete solvent fractions for ^{13}C -NMR study.

Figures 2 and 3 show the partial ^{13}C -NMR spectra of two monoaromatic isomeric octahydrophenanthrenes. The assignments for sym- H_8Ph have been discussed earlier (4). The appearance of new signals at 29 to 21.3 ppm is indicative of methyl groups in a variety of positions on saturated rings and are not present in sym- H_8Ph . The new signals between 30 and 35 ppm are indicative of five-membered rings being formed at the expense of the eight hydroaromatic carbons in the six-membered rings. The absence of a sharp line at approximately 14 ppm indicates that ring opening to a n-butyl substituent did not occur.

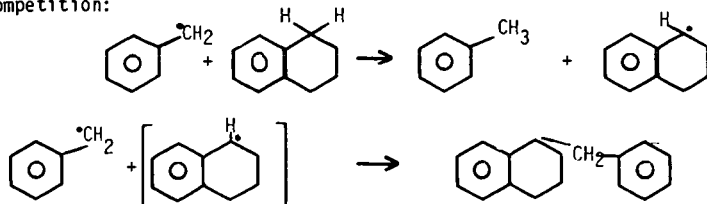
When an acceptor is present, the solvent products are more complex. Reactions were, therefore, performed with 1- ^{13}C -octahydrophenanthrene (10% ^{13}C). The presence of a label provided useful clues as to the real complexity of the structures and pathways for their formation. The products were separated by several liquid chromatographic steps into seven major fractions, arbitrarily designated A through G, and analyzed by ^{13}C -NMR, mass spectrometry, ultraviolet spectroscopy. The partial ^{13}C -NMR stick spectra are shown in Figure 4 where the label appears as an intense broken line. Table 1 illustrates some of the mass spectral data of these fractions. The "best fit" structures deduced from these data will be discussed.

Solvent Addition

The primary reaction between good donor solvents, such as tetralin and octahydrophenanthrene, and acceptors can give rather ideal products (ex. dibenzyl \longrightarrow toluene in 400-450°C range). However, when poor solvents are introduced secondary reactions become quite important (ex. mesitylene \longrightarrow polymers).

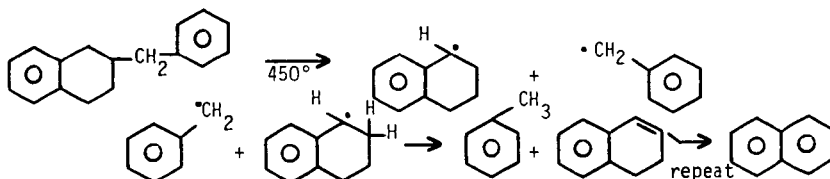
When reactions with oxygen-containing acceptors are performed in the 300-400°C region, the formation of solvent adducts occurs equally well with tetralin and mesitylene. Figure 5 shows a typical GLC curve for products from the reaction of benzyl alcohol and tetralin. These reactions were also done with D_4 -tetralin which permitted the firm identification of the solvent in the adduct. It is noted that several isomers of toluene-tetralin, as well as di-tetralin, were formed. Representative concentrates of total adducts were prepared by HPLC and GPC techniques which permitted their direct study by NMR, MS, and selective reactions.

These analysis indicated that at low temperatures free radical life-times can be reasonably long, thereby permitting competition between H[•] and C[•] for stabilization. The following equations illustrate one representation of this competition:



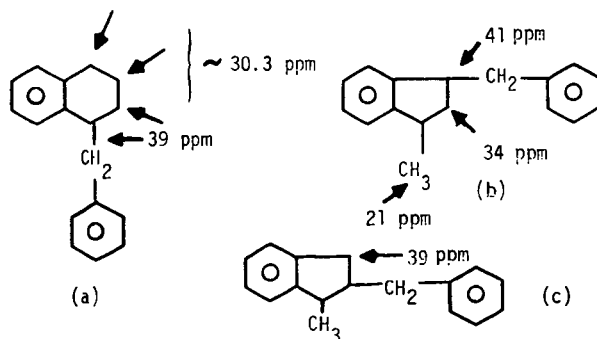
The benzyl free radicals can abstract hydrogen atoms leaving a carbon free radical which has the ability to combine with another benzyl radical. As the reaction proceeds, concentrations of both free radicals increase, creating a greater probability of adduction. Numerous analytical data show increasing concentration of adducts with reaction time and with increasing concentration of acceptor.

It appears that the formation of benzyl tetralin only occurs during the hydrogen transfer reactions at low temperatures (<400°C). If the adduct occurs as shown above, a certain degree of "depolymerization" could be achieved by isolating the adduct fraction and reacting it with fresh tetralin at 450°C. From the previous studies with dibenzyl, diphenylbutane, and phenylhexane, one would predict that cleavage would occur at 450°C as follows:



When this was done, less than 50% of the adduct "depolymerized." The remainder did not react. The remaining adducts had the same molecular weight but much larger M⁺-15 ions indicating the presence of a methyl group. ¹³C-NMR showed that significant rearrangement had occurred.

The following structures were deduced from the NMR spectra:



The strong line at 30.0 ppm in both spectra indicates that the six-membered ring is intact and that, when certain positions are substituted by benzyl groups, they resist cleavage. The fact that lines at 38, 39, and 41 ppm disappear upon heating at 450°C suggests that those particular structures are cleaved (unlikely if they are in a five-membered ring) or rearranged to a more stable form. Finally, the observation that benzyl naphthalenes are also present as reaction products confirms that isomer (a) is present and that it can still function as a donor after adduction.

The adduction reactions discussed are not limited to benzyl-type radicals nor to tetralin solvents. They have been observed with long chain thioether acceptors and donor solvents including dimethyltetralin, octahydro-phenanthrene, and tetrahydroquinoline. Donors using a D or ^{13}C label have been used to provide further confirmation that the solvent was incorporated in adducts.

CONCLUSIONS

Implications to Coal Liquefaction

Numerous implications on the fundamental chemistry of coal liquefaction can be drawn from the observed reaction of solvent isomerization and adduction. The literature indicates that recycle solvents from most coal liquefaction processes consist of 2 to 3 aromatic rings with various degrees of saturation, not unlike the model solvents studied. In this system, high levels of effective hydrogen donors can rearrange to isomers having poor donor quality. The following specific points are noted:

1. The isomerization of hydroaromatic donor solvents is a general phenomenon.
2. The rate of rearrangement appears to be first order with respect to donor solvent concentration. (The activation energy of the tetralin reaction is in the range of 26-32 Kcal/g-mole, depending upon whether a free radical precursor is present or not.)
3. The rate of isomerization increases with increasing number of hydroaromatic rings.
4. The rate of rearrangement is increased by order of magnitude when free radicals are present.
5. All solvents have the capability of becoming irreversibly adducted by acceptor free radicals which could arise from the coal.
6. The presence of oxygen and sulfur functions on the free radicals will enhance adduction. Adduction is also enhanced by long reaction times and low temperatures (<400°).
7. At high temperatures (>400°C), adducts are most likely to involve only poor donor solvents; high temperatures will not necessarily cleave adducts formed at low temperatures.
8. Solvent isomerization creates a basic problem in following the progress of liquefaction, namely, measuring the amount of transferred hydrogen. While it is possible to measure the level of "transferable hydrogen" (hydroaromatic six-membered ring

hydrogen) in the feed, recycle, or product liquids by ^{13}C -NMR (5), the present study suggests that it is not possible to isolate the portion contributing to hydrogen transfer alone.

REFERENCES

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- 1b. Benjamin, B.M., Raaen, V.F., Maupin, P.H., Brown, L.L., and Collins, C.J., Fuel 57, 269 (1978).
2. Cronauer, D.C., Jewell, D.M., Shah, Y.T., Modi, R.J., "Mechanism and Kinetics of Selected Hydrogen Transfer Reactions Typical of Coal Liquefaction," paper submitted to Ind. Eng. Chem. Fund., 1978.
- 3a. Ruberto, R.G., Cronauer, D.C., Jewell, D.M., Seshadri, K.S., Fuel 56, 17 (1977).
- 3b. Ibid., 25 (1977)
4. Seshadri, K.S., Ruberto, R.G., Jewell, D.M., Malone, H.P., Fuel 57, 111 (1978).
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Table I

MASS SPECTRAL DATA OF ISOLATED HYDROPHENANTHRENES

Isomer	186	184	182	180	178	171	169	167	158	154	141
-----m/e (% Base Peak)-----											
A	P (53)					P-15 (100)			P-28 (18.9)		
B	P ¹ (81)	P ² (34.7)				P ¹ -15 (100)			P ¹ -28 (37)		P ¹ -45 (35)
C	P ¹ (93)	P ² (98)				P ¹ -15 (63)					P ¹ -45 (100)
D			P (100)					P-15 (35)		P-28 (67)	P-41 (27)
E			P (100)					P-15 (27)		P-28 (69)	
F	P ² (23)	P ³ (10)	P ¹ (42)					P ¹ -15 (100)			P ¹ -41 (15)
G	P (100)					P-15 (76)			P-28 (56)		
Pure tetrahydro- phenanthrene			P (100)					P-15 (15)		P-28 (78)	P-41 (34)
Pure octahydro- phenanthrene	P (100)					P-15 (68)			P-28 (30)		P-45' (33)

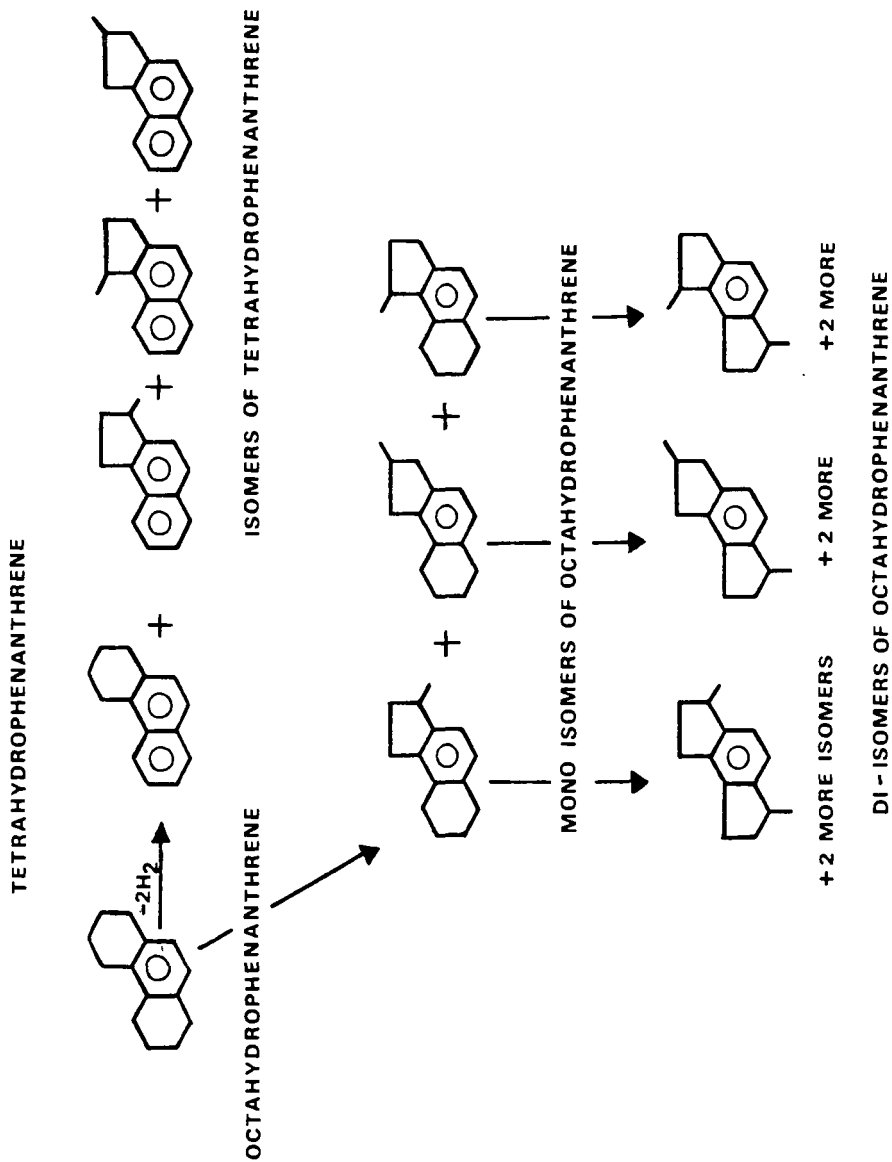


Figure 1: Reactions of Octahydrophenanthrene

Figure 2: ^{13}C -NMR spectrum of monomethyl isomers of rearranged octahydrophenanthrene

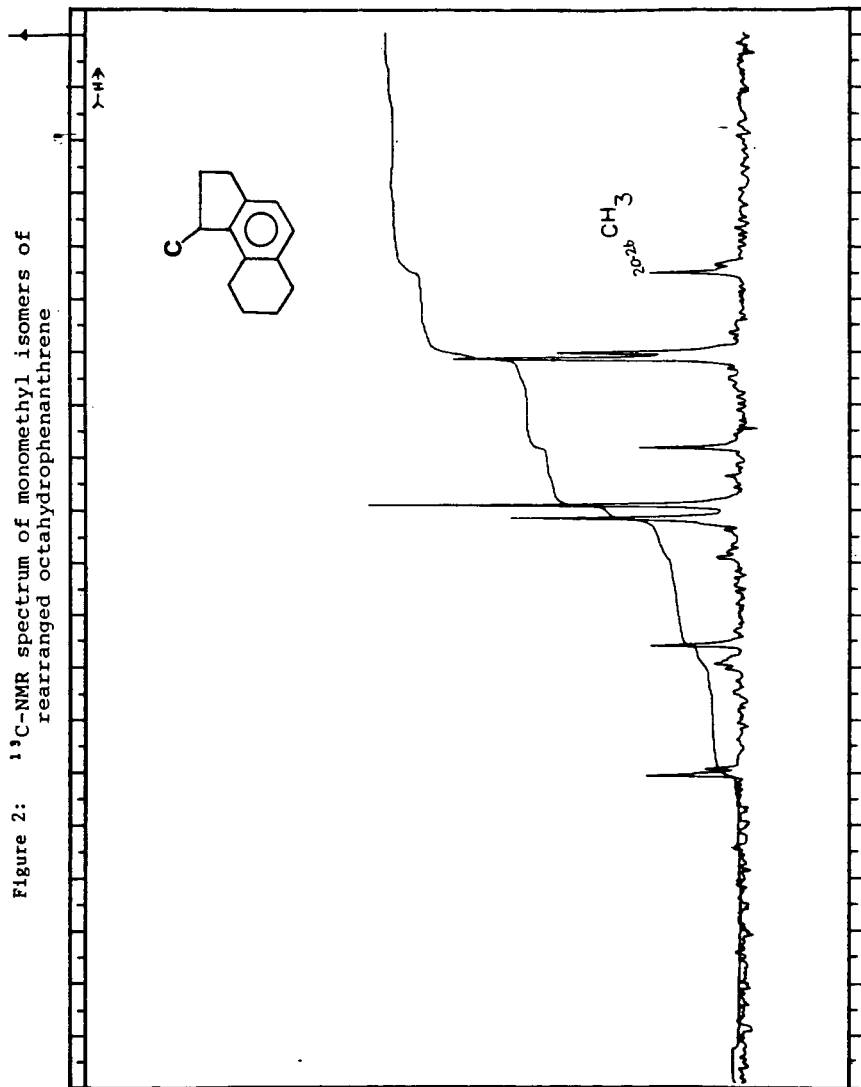
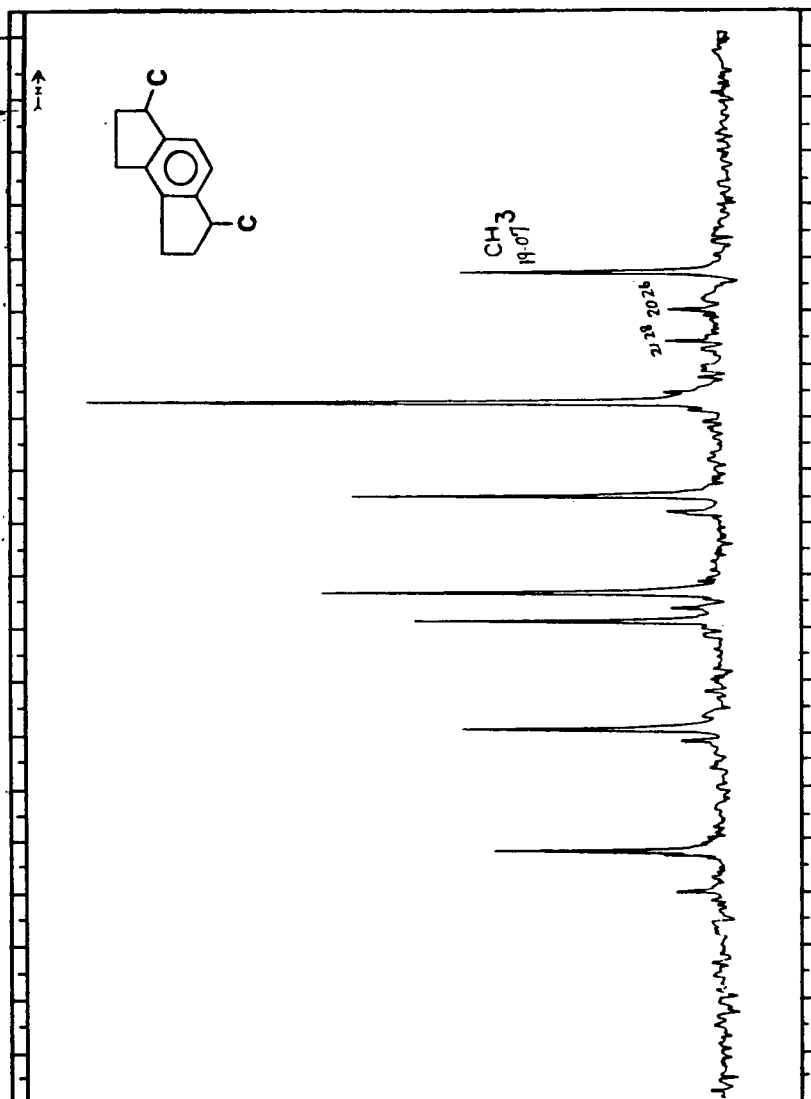


Figure 3: ^{13}C -NMR spectrum of dimethyl isomers of rearranged octahydrophenanthrene



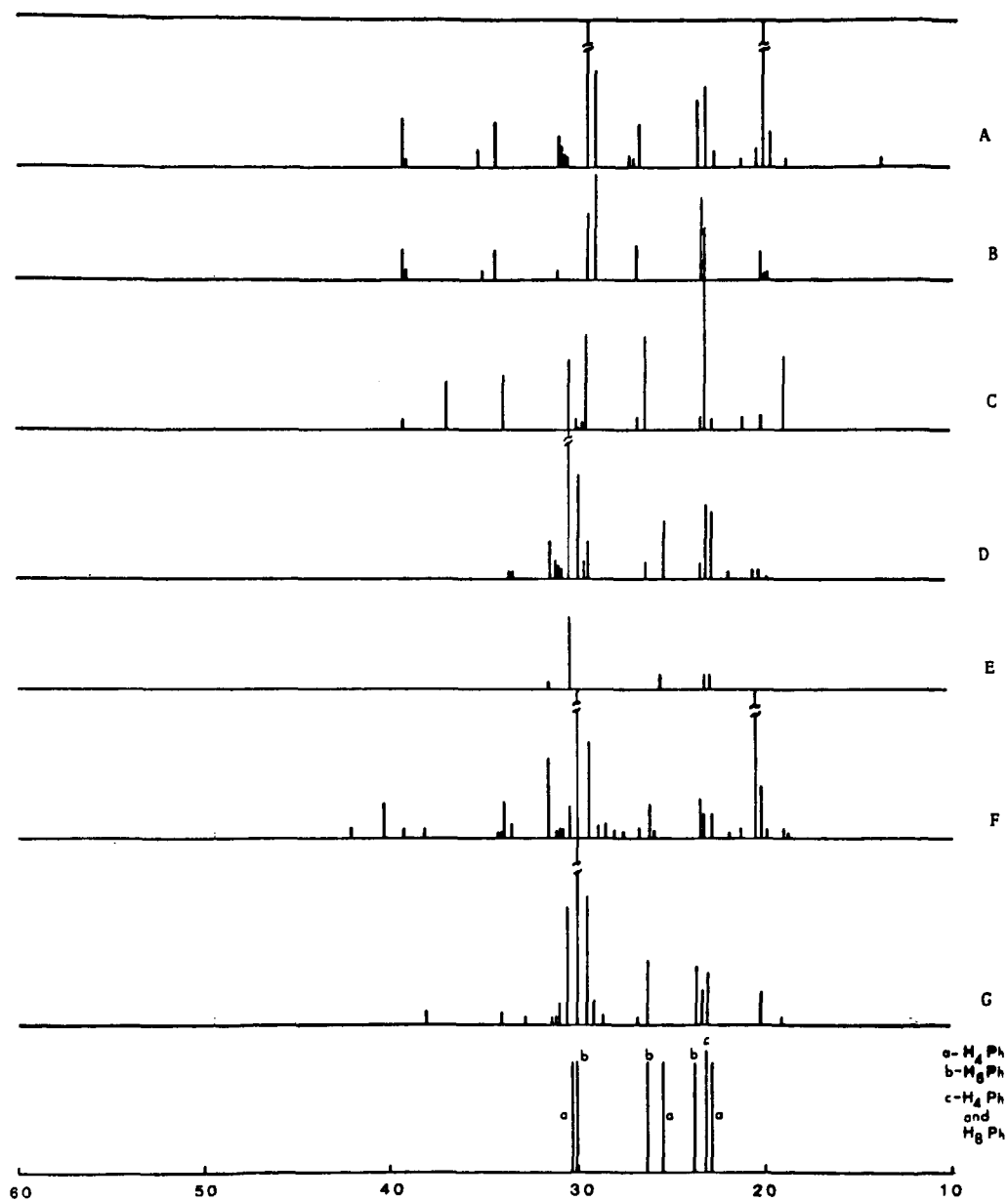


Figure 4: ^{13}C -NMR Spectra of Hydrophenanthrenes:
Saturate Region

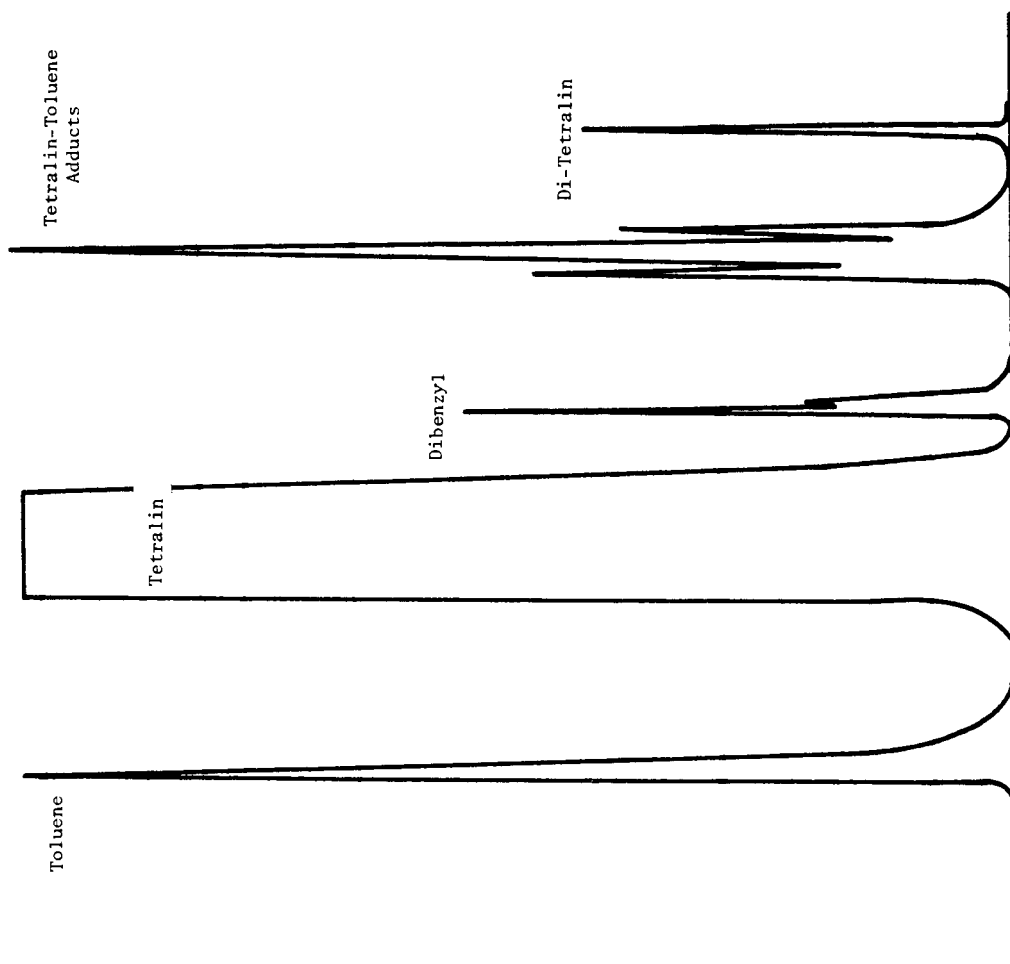


FIGURE 5: GAS-LIQUID CHROMATOGRAM OF PRODUCTS
FROM BENZYL ALCOHOL-TETRALIN REACTION
AT 400°C